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A SEARCH FOR HOST SENSITIZED LUMINESCENCE
OF RARE EARTH IONS IN $\text{Sr}_2\text{ZrP}_2\text{O}_9$

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A Search for Host Sensitized Luminescence

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by

N. T. Melamed and D. E. Harrison

Abstract

The compound $\text{Sr}_2\text{ZrP}_2\text{O}_9$ belongs to a family of host luminescent materials whose properties appeared to be favorable for the production of host-sensitized luminescence. However, measurements which were performed on this compound activated by rare earths indicated that little or no sensitization was taking place. An estimate of the expected sensitized luminescence yields indicates that the failure to obtain sensitization can be accounted for by the low oscillator strengths of the rare earth ions. It suggests that rare earth ions are in general not well suited as activators in host sensitized systems except at comparatively high concentrations.

I. Introduction

This paper describes some measurements aimed at observing host sensitized luminescence in the phosphor $\text{Sr}_2\text{ZrP}_2\text{O}_9$ (SZP) activated by rare earth ions. Sensitized luminescence is an important process in many phosphors⁽¹⁾, and it may be valuable in certain laser materials by providing means for improved pumping. In the non-photoconducting, inorganic phosphors sensitization is commonly achieved by the addition of impurities. Systems in which the host lattice serves as the sensitizer have not been well explored, and only a few investigations have been reported, notably by Botden, Botden and Kröger⁽²⁾, and Van Uitert et al⁽³⁾. All of these studies deal with alkaline earth tungstate or molybdate phosphors activated by rare earth ions.

SZP belongs to a family of host luminescent phosphors which has the generalized formula $\text{R}_2^{2+}\text{R}^{4+}\text{R}_2^{5+}\text{O}_9$, and whose properties are described in a recent paper⁽⁴⁾. Each member of this family has a well defined excitation band. By way of contrast, most other host luminescent materials including the tungstates and molybdates have very broad excitation bands resembling lattice absorption. This feature of SZP is particularly useful for the study of host sensitization by making it possible to clearly identify the region of optical absorption that corresponds to excitation of the sensitizer centers. In addition, SZP has low absorption coefficients in the host luminescent centers and long luminescent decay times. Both features characterize weakly allowed optical transitions, a situation favorable for sensitized luminescence. Preliminary measurements with SZP:Eu showed that europium emission occurred when the phosphor was excited in the SZP band, thereby raising the possibility that host sensitization was taking place.

Sensitized luminescence consists of the following steps⁽⁵⁾:

(1) absorption of energy in a center S, called the sensitizer, (2) relaxation of the lattice about the sensitizer, (3) transfer of energy from S to center A, called the activator; (4) relaxation of the lattice about the activator and, (5) emission of luminescence at center A. In the case of host sensitized luminescence, the lattice serves as the sensitizer and fulfills the requirements of step (1). The properties of sensitized systems are mainly determined by step (3), the energy transfer process. Several energy transfer mechanisms are discussed, notably by Dexter⁽⁵⁾ and in reviews by Klick and Schulman⁽¹⁾ and by Curie⁽⁶⁾. In SZP where photoconductivity does not play a role, the most probable energy transfer mechanisms are resonance transfer and cascade transfer.

In this study the presence of energy transfer was sought by measuring the wavelength dependence of the ratios of the intensity of the europium emission in SZP to the intensity of the emission of pure SZP. If the emission of the europium resulted mainly from excitation within the SZP band, then in the region where SZP was excited the excitation band for the europium emission would have the same shape as the excitation band for pure SZP. As a result the ratio of the europium emission to the SZP emission would remain constant over the portion of the wavelength range in which SZP is excited. If no transfer were taking place or if it were overshadowed by a more important excitation process this ratio would not be constant, but would most likely show a pronounced variation with excitation wavelength. This method seems especially suitable for the

detection of resonance or cascade transfer, since, for both processes, transfer takes place from the emitting state of the sensitizer after lattice relaxation about the sensitizer has occurred⁽⁵⁾. Consequently the transfer process involves a state of the sensitizer which has no memory of the wavelength that was used for excitation, providing that the shape of the sensitizer emission band is independent of the excitation wavelength. The transfer probability should therefore depend on the excitation wavelength in exactly the same way as does the probability of the sensitizer to emit in the absence of transfer and the ratio of the two should remain constant. The method is essentially equivalent to comparing independently determined excitation spectra, but by obtaining the ratio directly, errors due to fluctuations in conditions are minimized.

II. Experimental Procedure

$\text{Sr}_2\text{ZrP}_2\text{O}_9:\text{R.E.}$ compositions were prepared as described in reference (4) by the substitution of various rare earth ions for two atomic per cent strontium.

The experimental arrangement consisted of a Ferrand model 103420 grating monochrometer equipped with filters and illuminated by an H6, 1000 watt high pressure mercury arc lamp. This combination served as the source of variable monochromatic excitation. A Cary model 14 recording monochrometer recorded the relative shapes and magnitudes of the emission spectra produced at each excitation wavelength. The sample of SZP:R.E. and the reference powder of pure SZP were contained in separate 1/4" ultrasil quartz transmission cells. These were mounted on a rotating sample holder so that either sample or reference could be rotated into position while maintaining constant geometric and excitation conditions.

III. Experimental Results

The properties of the family of phosphors to which SZP belongs are described in reference (4). Pure SZP has a broad blue photoluminescence emission with a maximum at about 4900 Å which is due to the $(\text{ZrO}_x)^{Y^-}$ complex. The excitation spectrum extends from about 2300 Å to about 3400 Å, and shows structural details which are characteristic of the entire family. The excitation and emission spectra are shown in Fig. (1a) on an arbitrary scale of intensity.

The presence of rare earth ions in the lattice at a concentration of two atomic per cent markedly diminished the intensity of the blue SZP emission. The incorporation of either Eu, Sm, Dy, or Nd produced, in addition, new emission bands which were characteristic of the rare earth ions. In the case of Eu, this emission was generated when excited in the SZP band. Fig. 1b shows the emission of SZP containing 2 atomic % Eu, excited by 3650 Å radiation. Since 3650 Å radiation lies near the edge of excitation band of the SZP blue emission, it produces predominately Eu emission. Europium has three distinct emission bands in the visible spectrum: a very intense band in the blue region with a peak at 4410 Å, and a width at half maximum of about 400 Å, and two much narrower bands in the red, lying close to 5900 Å and 6115 Å. The true widths of the red lines are narrower than were actually measured. The recorded line widths were the result of poor instrument resolution due to the large slits which were necessary. A comparison of the Eu spectrum in SZP with that seen in other materials⁽⁷⁾ indicates that the blue emission arises from Eu^{2+} and the red

emission from Eu³⁺. Fig. 1c shows a typical emission spectrum obtained when the SZP:Eu phosphor is excited within the excitation band of pure SZP. It is evident that both the blue SZP emission and the Eu emissions are simultaneously present.

In Fig. 2 are plotted as a function of the excitation wavelengths the ratios of the intensities of the emissions occurring in SZP:Eu to the emission of pure SZP. Since absolute values were not required the intensities were not corrected for the spectral sensitivity of the detector.

IV. Discussion

Two important features are apparent in Fig. 2. First, the ratios obtained for the Eu emissions are anything but constant as a function of excitation wavelength. Indeed the wavelength dependence is so pronounced as to eliminate transfer as a dominant mechanism in the excitation of the Eu. The excitation of the europium which does occur within the SZP band is weak, and may be the result of other processes, primarily direct excitation into the europium centers. These processes overshadow any small amount of transfer which may be occurring within this region. Similar data collected for SZP:Sm and SZP:Dy also failed to yield evidence for appreciable transfer.

Second, and by way of contrast, the ratio of the SZP emission in SZP:Eu to that of pure SZP is substantially independent of excitation wavelength, within experimental error, and falls off only slightly at the long wavelength tail of the excitation band, where the absorption coefficient is very small and the errors increase. This result indicates that the shape of the excitation band of the SZP emission in SZP:Eu is not appreciably

altered by the addition of Eu, despite the fact that the quantum yield for the SZP emission is considerably lowered. In addition, the relative constancy of the SZP ratios supports the experimental method used to determine the existence of transfer, and provides a measure of the errors involved.

Having failed to observe significant energy transfer, it is worth inquiring into the reasons for its absence. In luminescent systems in which photoconductive processes do not play a role, the most likely transfer processes are either resonance transfer or cascade transfer. Resonance transfer yields can be calculated by means of an equation derived by Dexter⁽⁵⁾. Dexter's expression for the transfer probability, P_{sa} , for electric dipole interactions may be written in the following form:

$$P_{sa} = A \cdot \frac{Q_a}{R \tau_s} \int \frac{f(E) F(E)}{E^4} dE \quad (1)$$

where $A = \frac{3\kappa^4 C^4}{4\pi n^4} \left(\frac{\xi}{\xi_c} \right)^4$, n is the refractive index of the material, (ξ/ξ_c) is the ratio of the electric field strength within the crystal to that of an isolated atom, κ is the dielectric constant and Q_a is the strength of the activator absorption, measured as the area under the activator absorption band, R is the distance between activator and sensitizer, and τ_s is the lifetime for sensitizer emission.

The integral expresses the overlap between activator absorption and sensitizer emission, normalized so that $\int f(E) dE = 1$ and $\int F(E) dE = 1$.

Two important requirements for good transfer yields are immediately evident: good overlap, and strong activator absorption.

Dexter's expression may be used to estimate the transfer yield in the present system if it is assumed that the host luminescence of SZP originates in essentially localized, noninteracting centers, which may be regarded for the present purpose as resembling impurity centers. There are reasons for believing that this is a valid description. (4)

For SZP, whose refractive index is about 1.7, $A \approx 4.32 \times 10^{-21}$ (eV.cm)⁴ and we take $E = 3$ eV. Following Dexter, a good overlap of $f(E)$ with $F(E)$ would give a value of $\sim 1/3$ eV⁻¹. In order for transfer to occur, the transfer probability must equal or exceed the probability for sensitizer emission. Therefore

$$P_{sa} \tau_s = \frac{AQ_a}{E^4 R^6} > 1 \quad (2)$$

It remains to estimate Q_a ; $Q_a = \int \sigma_a(E) dE$, where σ_a is the absorption cross section of the activator. For a strong optical absorber having an allowed electric dipole transition, the oscillator strength, f , will be near unity and Q_a can be expected to be $\sim 10^{-16}$ (cm²e.V.). Rare earth absorptions appear to arise from phonon assisted electric dipole transitions. (8) The oscillator strengths are typically 10^{-6} , with f for Nd perhaps 10 to 100 times greater. Since Q_a is proportional to f , its value will be $\sim 10^{-22}$ (cm²e.V.).

Inserting these numerical values into (2), we find that

$$P_{sa} \tau_s = \left(\frac{3.48}{R} \right)^6 ,$$

where R is expressed in angstrom units. Thus, the activator-sensitizer distance R must be about 3.48 Å or less in order for efficient resonance transfer to occur.

It is almost certain that the R.E. ions substitute for Sr^{+2} . This assumption is supported by the behavior of Mn^{+4} which substitutes for Zr^{4+} and has almost no influence on the luminescence of SZP, in contrast to the effect of rare earth ion substitutions. The rare earth to $(\text{ZrO}_x)^{Y^-}$ ion distance is not known, but it is likely to be a nearest neighbor distance. Since the value of 3.48 Å is about the expected interatomic distance the only transfer likely to occur is at most between the rare earth ion and its nearest neighbors. In the case of host luminescence, where all the $(\text{ZrO}_x)^{Y^-}$ complexes are equivalent, this is tantamount to an increase in the optical cross section to include nearest neighbor ions. Since the number of $(\text{ZrO}_x)^{Y^-}$ complexes coordinating the europium ions is probably 8 or less, no more than 16% transfer can be expected in the samples containing 2 atomic % Eu. Unfortunately much higher concentrations of europium could not be prepared because of the limits of the SZP:Eu solid solution region.

A consideration of the terms which enter into the estimate of the resonance transfer yields, including the assumption of good overlap, suggests that the weak optical absorption coefficient of the rare earth ion is in itself sufficient to account for the low transfer yields. Even if the overlap were taken to be three times as large as we have assumed, the value of R would be increased to only 4.18 Å. Inasmuch as low optical transition probabilities are characteristic of rare earth ions and that

these are not likely to be greatly influenced by their environments, rare earth ions are not apt to be good activators in non-photoconducting host sensitized systems, except at activator concentrations of ~ 5 to 10%, or in special cases such as systems which have high sensitizer to sensitizer transfer probabilities.

The same conclusion is also valid for estimates of cascade transfer yields ^(1,9) since good activator-sensitizer overlap and strong activator absorption are equally important as the determining parameters. For photoconductive transport, which occurs in a different class of materials (e.g. SrS:Eu:Sm), different criteria must be applied.

It is understandable, therefore, why no transfer was observed in SZP:Eu, and why when excitation was confined to a spectral region where rare earth ion absorptions were forced to compete with host center absorption, the intensity of the rare earth emission was found to be 10 to 100 times smaller than when excited by 3650 Å.

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Figure Captions

Fig. 1 Excitation and emission spectra of SZP and SZP:Eu. 1a) Excitation and emission spectra of pure SZP. 1b) Emission spectrum of Eu in SZP:Eu under 3650 Å excitation. 1c) Emission spectrum obtained under 3000 Å excitation showing components of both Eu emission and SZP emission. In figures 1b) and 1c) the red Eu³⁺ lines are shown schematically.

Fig. 2 Ratios of the different emissions seen in SZP:Eu to the emission of pure SZP obtained at various wavelengths under similar conditions of excitation. The ratios are of the intensities at the peak wavelength for each emission. They are not corrected for the widths of the emission bands nor for the detector sensitivity, and therefore do not represent relative quantum yields.

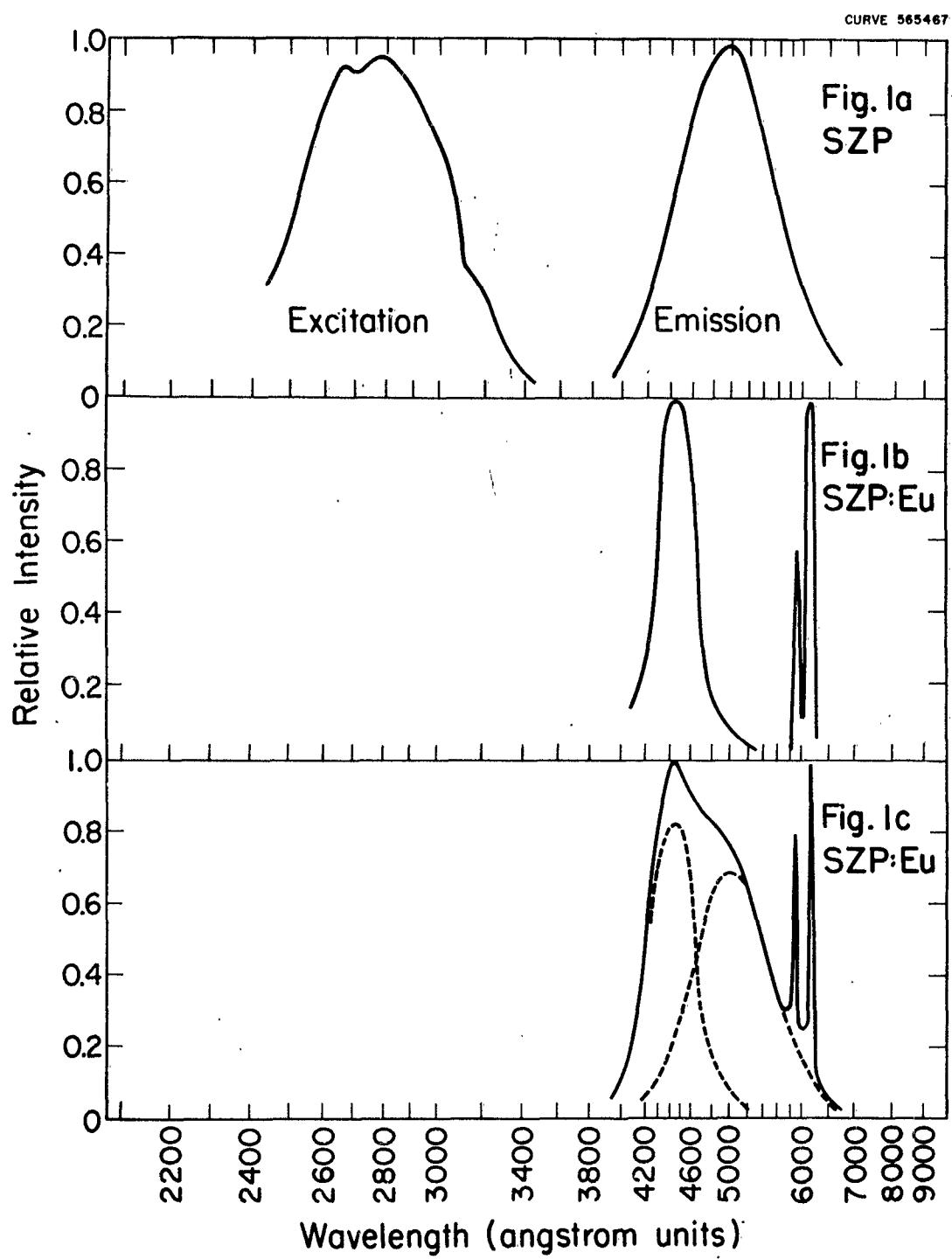


Fig. 1

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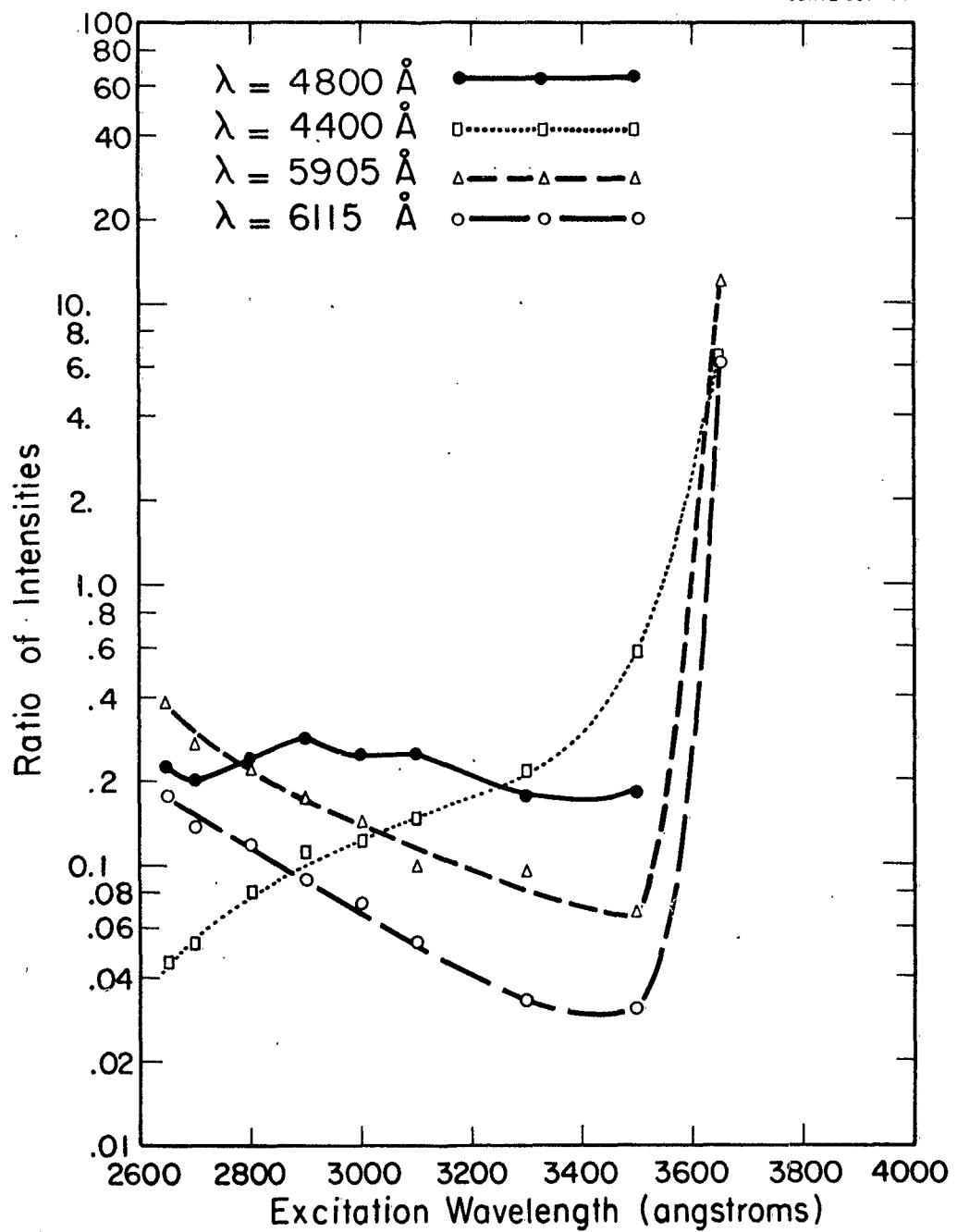


Fig. 2

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